

Available online at www.sciencedirect.com



Journal of Hazardous Materials

Journal of Hazardous Materials 147 (2007) 325-333

www.elsevier.com/locate/jhazmat

Investigation on the rapid degradation of congo red catalyzed by activated carbon powder under microwave irradiation

Zhaohong Zhang^{a,*}, Yabo Shan^a, Jun Wang^b, Hongjie Ling^a, Shuliang Zang^b, Wei Gao^a, Zhe Zhao^a, Huachun Zhang^a

> ^a Department of Environment Science, Liaoning University, Shengyang 110036, PR China ^b Department of Chemistry, Liaoning University, Shengyang 110036, PR China

Received 22 July 2006; received in revised form 22 November 2006; accepted 31 December 2006 Available online 12 January 2007

Abstract

Azo dyestuff-congo red in aqueous solution can be degraded rapidly under microwave irradiation in the presence of activated carbon powder. The results showed that the degradation ratio could reach 87.79% for 25 mL total volume with 50 mg/L congo red and 2.0 g/L activated carbon powder under 1.5 min microwave irradiation. Furthermore, within the same irradiation time, congo red could be degraded fully by increasing addition amount (e.g. 3.6 g/L) of activated carbon powder and the degradation ratio was up to 96.49%. Otherwise, with the same addition amount, congo red also could be degraded completely by prolonging irradiation time (e.g. 2.5 min) and the degradation ratio was up to 97.88%. In addition, the influences of microwave irradiation time, initial concentration of congo red, addition amount and used times of activated carbon powder as well as solution acidity on the degradation were discussed in details adopting UV–vis spectra, FT-IR spectra, ion chromatography, high phase liquid chromatography (HPLC) and TOC analysis technologies. Here, the method using activated carbon powder as catalyst under microwave irradiation ratios, short reaction time, low costs, no intermediates and no secondary pollution. Therefore, it may be fit for dealing with various azo dyestuff wastewaters on a large scale.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Activated carbon powder; Microwave irradiation; Rapid degradation; Congo red

1. Introduction

In general, the treatment of various dye wastewaters has been regarded to be one of the main aims in controlling environmental pollution all over the world [1,2]. Since most of organic dye compounds ordinarily contain benzene and naphthalene rings, they cannot be decomposed easily by conventional biological and chemical methods [3–7]. In particular, as well known, earlier studies showed that the biological method was carried out under the strict conditions [8,9]. And as one of popular chemical methods, the photocatalytic degradation generally needs long irradiation time and displays halfway degradation [10,11]. Furthermore, sometimes some intermediates such as benzene and aniline derivatives, which are considered to be mutagen, mitotic poisons and suspected carcinogens, may form during

0304-3894/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2006.12.083

degradation process of the organic pollutants in dye wastewater [12,13]. Therefore, it is urgent to seek for the novel technologies to degrade various organic pollutants effectively and completely.

Recent years, there have been some reports with respect to wastewater treatment using microwave-assisted approaches. For example, the wet air oxidation on the activated carbon under microwave irradiation was used in treating phenolic wastewater [14]; the continuous flow mode on the activated carbon fixed bed was used for microwave-assisted degradation of concentrated *p*-nitrophenol [15]; the microwave irradiation was used for enhancing a series of advanced oxidation processes in the degradation of 4-chlorophenol [16]. Hence, the application of microwave technology has been attached more and more importance to treating environmental pollutants.

The frequency range of microwave, a kind of electromagnetic wave, is from 300 MHz to 300 GHz, that is, the wavelength lies between 1.0 mm and 1.0 m. And it has very strong penetrating ability in many media. The microwave irradiation can

^{*} Corresponding author. Tel.: +86 24 62205173; fax: +86 24 62202380. *E-mail addresses:* zzhlyl@163.com, lnuhjhx@sina.com (Z. Zhang).

make the polar molecules in solution rotate fleetly, which brings obvious heat effects. At the same time, it can further change the thermodynamics function and reduce the activation energy of the reaction system, and weaken the chemical bond intensities of various molecules [17]. Moreover, the existence of microwave absorbent can increase these effects. Therefore, the technology of microwave irradiation integrated with some suitable microwave absorbents as catalysts should be even more suitable for treating dye wastewaters.

As well known, the role of the activated carbon powder may be demonstrated in two aspects, namely, adsorbent and microwave absorbent [18–20]. As adsorbent the activated carbon powder can remove many organic and inorganic pollutants from solution. As microwave absorbent, the activated carbon powder can strongly absorb microwave energy. Due to the nonuniformity, the "hot spots" on the surface of activated carbon particles may be generated, where the temperatures are out and away higher than those of other positions, and chemical reactions may take place easily.

In this study, the microwave technology reported previously was improved and simplied, and a rapid and simple method treating dye wastewater was presented. Here, the azo dyestuff-congo red, because of representability and easy monitoring, as a model compound under microwave irradiation in the presence of activated carbon powder as microwave absorbent was investigated in details. The influences of irradiation time, initial concentration of congo red, the addition amount of activated carbon powder and solution acidity on the degradation were discussed, respectively. This technology revealed many advantages such as high degradation ratio, short irradiation time, simple equipments, low costs, no intermediates and no secondary-pollution, so the good and extensive application foregrounds were revealed.

2. Experimental

2.1. Materials

Congo red (Analysis purity, Shanghai Chemistry Reagent Corporation, China) was purchased, and its structure is shown in Plate 1. The granular activated carbon (GAC) (Liaoning Medical Company, China) was used as a catalyst. It was made from coal, with ash content 3-5%, particle size 2-3 mm, surface area $1300 \text{ m}^2/\text{g}$ and average pore diameter 2-3 nm. Water purified by a Milli-Q water system (Millipore Company, USA) was used throughout the experiment.

2.2. Apparatus

Cary-50 UV–vis spectrometer (Varian Company, USA), ICS-90 ion chromatography apparatus (Dionex Company, USA), Pro-210 high phase liquid chromatography (HPLC) apparatus (Varian Company, USA), Nicolet Avatar 330 Fourier transform infrared (FT-IR) spectrometer (Nicolet Company, USA) and Liqui TOC apparatus (Elementar Analysensysteme GmbH Company, Germany) were used to inspect the degradation processes of congo red. G8023ESL-V8 controllable microwave oven (Guangdong Galanz Company, China) was adopted to irradiate the congo red solutions, operating at microwave frequency of 2450 MHz and output power of 800 W. pHS-3C pH meter (Shanghai Leici Company, China) was used to determine acidities of the congo red solutions.

2.3. Pretreatment of activated carbon powder

For high catalytic activity, firstly, GAC were properly triturated and sifted out using 100 mesh sieve, and then the powdery activated carbon (PAC) was obtained. 10.00 g activated carbon powder was weighted and put into 100 mL deionized water, then, boiled for 30 min. After cooling to the room temperature, the activated carbon powder was filtered out. This operation procedure was repeated three times. Afterwards, the activated carbon powder was dried at 105 °C for about 6.0 h to constant weight and stored in a desiccator for use. It is noticeable that the granularity of activated carbon powder should not be excessively small for easy separation and high catalytic activity.

2.4. Experimental method

The 25 mL prepared congo red solution (50 mg/L) and treated activated carbon powder (2.0 g/L) were put into a self-made glass reactor. As shown in Plate 2, in order to prevent volatilization of the solvent a condenser was jointed on the glass reactor. Afterwards, the apparatus was installed in the microwave oven. The pH value of the suspension was adjusted to 8.0. The microwave was utilized to irradiate this suspension. After 1.5 min, the UV–vis spectra of filtered congo red solution (diluted by five times) were determined in the wavelength range from 190 to 800 nm. In order to compare the degradation effects, the UV–vis spectra of the treated congo red solutions by one-fold microwave irradiation and one-fold activated carbon powder, respectively, were also given in Fig. 1. The maximal absorbencies of 0–40 mg/L congo red solutions abide by Lambert-Beer's law.



Plate 1. Structure of congo red molecule.



Plate 2. Schematic illustration of experimental apparatus: (1) microwave generator; (2) reaction solution; (3) activated carbon powder; (4) condenser; (5) time display; (6) time adjuster; (7) power adjuster.

The calibration curve (A = 0.04022C (mg/L), $R^2 = 0.9961$) of standard congo red solution was used to estimate the degradation ratio. The degradation ratio was calculated by the following equation: degradation ratio (%) = $[(C_0 - C_t)/C_0] \times 100\%$, where C_0 represents the initial concentration, C_t represents the instant concentration. Table 1 gives the reduction ratios (%) of the absorption peaks of congo red solution at different characteristic wavelength. The degradation ratio of congo red at intervals of 0.5 min within 2.5 min was shown in Fig. 2. The relation of $-\ln(C_t/C_0)$ and irradiation time (t) was shown in Fig. 3, which can infer the kinetics of degradation reaction.

For further validating degradation of congo red in aqueous solution, the ionic chromatogram and HPLC were determined as shown in Figs. 4 and 5, respectively. During determination of ionic chromatogram, the initial concentration of 50 mg/L congo red and irradiation time of 0.5, 1.5 and 2.5 min were



Fig. 1. UV-vis spectra of congo red solution under different conditions: (a) original solution; (b) one-fold microwave; (c) activated carbon; (d) microwave + activated carbon.

Table 1	
Reduction ratio (%) of various absorption peaks of congo red ^a	

Reduction ratio (%)	A (499 nm)	<i>B</i> (345 nm)	C (236 nm)	Average (%)
Original solution (a)	0	0	0	0
One-fold microwave (b)	2.92	2.65	2.31	2.63
Activated carbon (c)	26.56	26.49	28.38	27.14
Microwave + activated carbon (d)	89.15	87.42	86.79	87.79

^a For microwave irradiation the reduction ratio is equal to degradation ratio; for activated carbon the reduction ratio is equal to adsorption ratio.



Fig. 2. Influence of irradiation time on degradation ratio: (\blacktriangle) microwave + activated carbon (499 nm); (\blacklozenge) microwave + activated carbon (345 nm); (\blacksquare) microwave + activated carbon (237 nm); (\bigcirc) one-fold activated carbon (499 nm); (\bigcirc) one-fold microwave (499 nm).

adopted. The other conditions were as follows: AS9-HC column (250 mm \times 4 mm i.d.), 9.0 mmol/L NaCO₃ eluent, 1.0 mL/min flow rate and conductivity detector. For the determination of HPLC, the initial concentration of 200 mg/L and irradiation time



Fig. 3. Kinetics of degradation reaction of congo red (at 499 nm): (\blacktriangle) microwave + activated carbon; (\bigcirc) only activated carbon; (\bigcirc) only microwave.



Fig. 4. Ion chromatogram of congo red solution during degradation: (a) 0.5 min; (b) 1.5 min; (c) 2.5 min.

of 1.0, 2.0 and 3.0 min were adopted. The other conditions were as follows: C18 (250 mm \times 4.6 mm i.d.) reverse phase column, 0.3:0.7–1.0:0.0 proportion of ethanol and water, 1.0 mL/min flow rate and UV detector (at 236 nm wavelength). Otherwise, total organic carbon (TOC) values of treated solution were also determined. For 50 mg/L congo red solution, the irradiation time of 1.5 and 2.5 min were adopted. The carrier gas was oxygen of 0.95–1.00 bar. The other conditions were as follows: max temperature 850 °C, 200 mL/min flow rate and IR detector.

The influences of the initial concentrations (10–90 mg/L) of congo red solution, addition amounts (0–3.6 g/L) of activated carbon powder, and initial pH (4.0–12.0) of the solution on the degradation were reviewed, respectively, in this work. These results were showed in Figs. 7–9, respectively. In addition, in order to validate that all congo red in aqueous solution were degraded under microwave irradiation catalyzed by activated carbon powder, FT-IR spectra of used activated carbon powder

were determined in the wavelength range from 400 to 4000 cm^{-1} as shown in Fig. 6. For comparison, the FT-IR spectrum of the original congo red was also given in Fig. 6. At last, for reviewing the catalytic activities of reused activated carbon powder the degradation of congo red within 1.5 min irradiation were also investigated and the results were shown in Fig. 10. All confirmed conditions were used throughout experiment if there was not special demonstration.

3. Results and discussion

3.1. UV-vis spectra of congo red solution during degradation

Fig. 1 shows that the congo red solution gives three absorption peaks at 499 nm (A), 345 nm (B) and 236 nm (C), respectively, in UV-vis spectra. At the beginning, it could be found that all absorption peaks went down slightly even under one-fold microwave irradiation in the absence of any catalyst, which indicated that only a little of congo red could be degraded. And when one-fold activated carbon powder existed, all absorption peaks also went down to a certain extent synchronously. It indicated that the activated carbon powder could adsorb some congo red dyes in a way, but the most still left over in the solution except adsorbed congo red. Nevertheless, all absorption peaks of congo red solution fell to a large extent with a bit shift under microwave irradiation in the presence of activated carbon powder. It could also be seen from Fig. 1 that the reduction ratio of absorption peak (C) belonging to the naphthalene rings of congo red was only 2.31% within 1.5 min microwave irradiation, which meaned that it was difficult for the naphthalene rings to degrade only under microwave irradiation without any catalyst. However, the reduction ratio of absorption peak (C)could reach 86.79% in the presence of activated carbon powder under microwave irradiation within the same irradiation time. So great reduction ratio indicated that the naphthalene rings of congo red could be degraded easily in the presence of activated carbon powder under microwave irradiation.



Fig. 5. HPLC of congo red solution during degradation (at 236 nm): (a) 1.0 min; (b) 2.0 min; (c) 3.0 min.



Fig. 6. FT-IR spectra of congo red at different conditions: (a) original congo red; (b) congo red adsorbed on activated carbon; (c) 3.0 min microwave irradiation; (d) 5.0 min microwave irradiation.

All results reveal that the activated carbon powder has obvious catalytic activity for degradation of congo red under microwave irradiation. Hence, it is known that the activated carbon powder mainly displays strong catalytic activity under microwave radiation except its adsorption ability. The research results show the degradation process in the presence of activated carbon powder with microwave irradiation is different from that of photocatalytic degradation through •OH radical [21,22]. On the one hand, in general, the photocatalytic degradation needs long irradiation time, while the microwave degradation with activated carbon powder occurs rapidly, and it needs only several minutes. On the other hand, a number of intermediate products were usually formed during photocatalytic degradation. Contrarily, there are few intermediate products under microwave radiation in the presence of activated carbon powder. It indicates that whole congo red molecule can burn adequately and then be eliminated thoroughly from solution once it touches the "hot spots" on the surface of activated carbon particles.

3.2. Influence of irradiation time on degradation ratio and reaction kinetics

As shown in Fig. 2, the change of degradation ratio with irradiation time was reviewed for 25 mL suspension of 50 mg/L congo red and 2.0 g/L activated carbon powder. The case under one-fold microwave irradiation was also considered. It could be observed that the degradation ratio increased rapidly with increasing irradiation time in the presence of activated carbon powder. And the degradation ratios calculated based on three absorption peaks (A, B and C) reached 97.88%, 95.55% and 92.90%, respectively, under 2.5 min microwave irradiation. It could be known that, under such conditions, the congo red was degraded remarkably. Nevertheless, for one-fold microwave irradiation the average degradation ratio corresponding to three absorption peaks (A, B and C) was only 3.70%. Of course, the activated carbon powder can adsorb a part of congo red from solution too, but the saturated adsorption ratio was not higher

than 27.20%. As shown in Table 1, the degradation ratio under microwave irradiation in the presence of activated carbon powder was much higher than the sum of degradation ratio from one-fold microwave irradiation and the adsorption ratio from one-fold activated carbon powder. These results indicate that the reduction of congo red mainly results from the combined function of microwave irradiation and activated carbon powder, but not a simple addition of both.

The studies on the reaction kinetics of three courses were also carried out and the results were shown in Fig. 3. It was found that the degradation reaction of congo red under microwave irradiation in the presence of activated carbon powder basically belonged to first-order reaction kinetics. Its rate constant $(1.5138 \text{ min}^{-1})$ was far beyond those $(0.1213 \text{ and } 0.0296 \text{ min}^{-1})$ corresponding to the degradation reaction of one-fold microwave irradiation and the adsorption process of one-fold activated carbon powder, respectively, which also belonged to first-order reaction kinetics.

In addition, the calculated reduction ratios according to the determination of TOC values were 73.71% and 86.13%, respectively, under 1.5 and 2.5 min microwave irradiation. These results also demonstrated that the congo red in the treated solution could mostly be degraded under microwave irradiation in the presence of activated carbon powder.

3.3. Ionic chromatogram and HPLC of congo red solution during degradation

In order to confirm the degradation extent of congo red and the formation of intermediate products during degradation, the ionic chromatogram and HPLC were also determined, respectively, at different irradiation time. The results were shown in Figs. 4 and 5, respectively. It could be observed in Fig. 4 that the ionic chromatographic peaks corresponding to NO_3^- and SO_4^{2-} anions gradually increased along with microwave irradiation, while the peak corresponding to NO_2^- anion continually decreased. All of these results indicated that the C–S, C–N and azo bonds in the congo red molecule were destroyed gradually. The sulfur and nitrogen atoms were oxidized and transferred into NO_2^- , NO_3^- and SO_4^{2-} anions, respectively, but the NO_2^- anion finally was oxidized to the NO_3^- anion. This was the reason why the peak corresponding to NO_2^- anion decreased. By all means, the congo red in aqueous solution could be mineralized to a series of simple and innocuous inorganic ions in the end under microwave irradiation in the presence of activated carbon powder.

Additionally, it was showed in Fig. 5 that the matrix peak of the congo red molecule at 10.847 min retention time minished little by little with microwave irradiation. It meaned the naphthalene rings of congo red were destroyed by degrees, and then disappeared at last. Otherwise, a new peak appeared at 12.257 min retention time under 1.0 min microwave irradiation, which indicated a small quantity of intermediate products formed. But it disappeared immediately under 3.0 min microwave irradiation. The results demonstrated that the congo red and its intermediate products in aqueous solution could be degraded thoroughly after 3.0 min microwave irradiation in the presence of activated carbon powder, though intermediate products once formed during the degradation.

3.4. FT-IR spectra of congo red on the surface of activated carbon powder

To review the degradation behave of congo red on the surface of activated carbon particles, the FT-IR spectra of the used activated carbon powder was determined as shown in Fig. 6. It could be seen clearly that some characteristic absorption peaks of congo red appeared in Fig. 6b, which indicated that a mass of congo red was adsorbed on the surface of activated carbon particles. According to the decrease of characteristic absorption peaks in Fig. 6c, it was known that the amount of congo red adsorbed on the surface of activated carbon particles reduced under 3.0 min microwave irradiation. After 5.0 min, the characteristic absorption peaks of congo red disappeared almost in Fig. 6d, which indicated that most of congo red dyes on the surface of activated carbon were degraded or desorbed. Based on the analysis of UV-vis spectra and TOC values mentioned above, not only the congo red dyes adsorbed on the surface of activated carbon were degraded under microwave irradiation, but also those in the solution were done. Perhaps, the congo red in the solutions may firstly be adsorbed on the surface of activated carbon particles, and then, they are immediately degraded under microwave irradiation. And it cannot only rest on the adsorbed stage.

3.5. Influence of initial concentration on the degradation ratio

A series of congo red solutions with different initial concentrations ranging from 10 to 90 mg/L were used for studying the influence on the degradation ratio within 1.5 min microwave irradiation. As shown in Fig. 7, the degradation ratio under microwave irradiation in presence of activated carbon powder maintained above 96% before 30 mg/L concentration. And then



Fig. 7. Influence of initial concentration of congo red on degradation ratio (at 499 nm): (\blacktriangle) microwave + activated carbon; (\bigcirc) one-fold activated carbon; (\bigcirc) one-fold microwave.

it decreased gradually with increasing concentration. However, the adsorption ratio in the presence of one-fold activated carbon powder decreased all through. It means that the adsorption ability of activated carbon powder is limited for congo red. Otherwise, for one-fold microwave irradiation the degradation ratio of congo red was very low throughout the experimental concentration range.

These results revealed that the elimination effects under microwave irradiation in presence of activated carbon powder were much better than those of both one-fold microwave irradiation and one-fold activated carbon powder. It was proved again that the degradation of congo red mainly resulted from the combined action of microwave irradiation and activated carbon powder, but not a simple addition of the degradation of one-fold microwave irradiation and the adsorption of one-fold activated carbon. In addition, for high concentrated congo red solution (above 50 mg/L) the activated carbon powder also exhibited relatively high catalytic activity under microwave irradiation. Only when the concentration of congo red increased continuously, the catalytic activity of activated carbon powder decreased a little. Of course, it was obvious that the low initial concentration was benefit for degradation of congo red. For a large number of congo red molecules the catalytic degradation ability of activated carbon powder became relatively low.

3.6. Influence of addition amount of activated carbon powder on the degradation ratio

In general, the addition amount of catalyst is a very important parameter in treating wastewater for both photocatalytic and sonocatalytic degradations [23–25]. Similarly, in order to optimize the addition amount of activated carbon powder as catalyst for high degradation ratio, the influences of different addition amount from 0.4 to 3.6 g/L were also considered. As shown in Fig. 8, the degradation ratio of congo red showed a rapid increasing trend before addition amount of 2.0 g/L activated carbon powder, and then went up slowly. This phenomenon could be explained as the mutual screen among activated carbon particles for high addition amount. The degradation ratio could be up to 96.49% for 3.6 g/L addition amount of activated carbon under



Fig. 8. Influence of addition amount of activated carbon powder on degradation ratio (at 499 nm): (\blacktriangle) microwave + activated carbon; (\bigcirc) one-fold activated carbon.

1.5 min microwave irradiation. It could also be seen that the adsorption ratio became high with increasing addition amount of activated carbon powder, but the increasing extent was small and it was only 35.66%. The above results testified again that the decrease of congo red in aqueous solution was mainly owing to the degradation under microwave irradiation in the presence of activated carbon powder.

3.7. Influence of acidity on the degradation ratio

The influences of acidities on the degradation of congo red were studied in the range between pH 4.0 and pH 12.0. The results were shown in Fig. 9. It was found that the degradation ratio of congo red under 1.5 min microwave irradiation in the presence of activated carbon powder changed scarcely and maintained a high level from pH 4.0 to pH 8.0, and then fell slightly after pH 8.0. Afterwards, it began to go up somewhat after pH 10.0 again. The similar change regulars were also observed for the adsorption of one-fold activated carbon powder and the degradation ratio of congo red under microwave irradiation. In any case, the degradation ratio of congo red under microwave irradiation.



Fig. 9. Influence of pH value on degradation ratio (at 499 nm): (\blacktriangle) microwave + activated carbon; (\bigcirc) one-fold activated carbon; (\bigcirc) one-fold microwave.



Fig. 10. Influence of reused times on degradation ratio (at 499 nm).

ation in the presence of activated carbon powder was obviously higher than the adsorption ratio of one-fold activated carbon and degradation ratio of one-fold microwave irradiation.

In general, the acidity can influence the distribution and quantity of the charges on the surface of activated carbon particles. When the pH value is lower than isoelectric point (pH 6.38) of activated carbon, its surface is positively charged, whereas its surface is negatively charged when the pH values is higher than the isoelectric point. The congo red molecule with two sulfonic groups ionizes easily even though in strong acidic solution and then becomes a soluble congo red anion. Therefore, in the acidic and neutral solution the congo red anions are close to the surface of activated carbon particles or adsorbed on it with positive charges. These congo red anions can be oxidized directly by oxygen in aqueous solution under microwave irradiation. Hence, before pH 8.0, the results exhibited a high degradation ratio of congo red. However, at higher pH values the congo red anions were generally excluded away from the charged negatively surface of activated carbon particles, so the degradation ratio began to decrease. Furthermore, the reason that the degradation ratio increased slightly in alkali solution may be the occurrence of partial radical oxidation degradation. This is because a number of OH⁻ anions loss their electrons at high temperature and transfer into •OH radicals which also have strong oxidation ability. Because the degradation ratio relates to the pH values in solution, the treatment of some organic pollutants like congo red dye should be carried out in the acidic or neutral solution under microwave irradiation in the presence of activated carbon powder.

3.8. Influence of used times of activated carbon powder on the degradation ratio

As known to all, the important one for any catalyst is recycle. Here, the catalytic activities of reused activated carbon powder were also studied. It was found that the used activated carbon powder could be separated easily from the treated solution. The used activated carbon powder was washed out and rehandled adopting the pretreating method in experiment part, and then reused in the new experiments with fresh congo red solution. As shown in Fig. 10, comparing with the new activated



Fig. 11. Possible principle of degradation on the surface of activated carbon on ratio.

carbon powder, the catalytic activity of used activated carbon powder became low gradually along with used times. Although the declined extents became smaller and smaller after several times and maintained a stable level, the catalytic activity wholly decreased about 50% comparing with the new one. It was indicated that the activated carbon itself could also be destroyed synchronously to a certain extent during degradation of organic pollutants under microwave irradiation. This process results in the catalytic activities of reused activated carbon powder going down considerably. Although a great number of organic pollutants can be effectively mineralized under microwave irradiation with activated carbon powder, the reclamation and reuse of it are still an urgently solved problem for widely adopting this method in practical application.

3.9. Principle on microwave degradation of congo red

In present, there are two popular points of view on the fact that the microwave irradiation can accelerate the elimination of organic pollutants in the presence of activated carbon, that is, microwave-assisted oxidation and microwave-assisted adsorption. Although the investigation on the microwave degradation in the presence of activated carbon powder has not been reported too much yet, based on our studies we are inclined to the former. It was thought that the mechanism or process of microwave degradation of organic pollutants in the presence of activated carbon powder should be explained as the formation of "hot spots" and oxidation combustion of organic pollutants. As shown in Fig. 11, when the activated carbon particles as microwave absorbent are irradiated by microwave, their uneven surfaces will absorb these microwave energies, and a lot of "hot spots" form synchronically. The temperature of these "hot spots" can ordinarily reach 1200 °C above. Due to the functions of both thermal and non-thermal effects, not only the azo bonds of congo red can be destroyed completely but also the naphthalene rings of it can be degraded rapidly. According to the determination of TOC, it is considered that this process is almost equal to oxidation combustion of organic pollutants. CO₂ and H₂O are given out and various simple inorganic ions are also produced, so that the congo red as well as intermediate products in aqueous solution are degraded fully at last.

4. Conclusion

When the treated activated carbon powders are adopted as catalyst and the microwave is used as irradiation source, the organic pollutants like congo red in aqueous solutions can be degraded rapidly and totally. In present work, the congo red as a model compound was firstly degraded adopting the technology of microwave irradiation integrated with activated carbon powder. For a high degradation ratio of congo red the optimized conditions were considered to be initial concentration of 50 mg/L congo red, addition amount of 2.0 g/L activated carbon powder, microwave irradiation of 800 W output power and 2450 kHz frequency and pH 8.0. Under such conditions, the degradation ratio could reach 89.15% for 25 mL congo red solution within 1.5 min. In addition, the degradation ratios reached 96.49% and 97.88%, respectively, by appropriately increasing addition amount (e.g. 3.6 g/L) of activated carbon powder and prolonging irradiation time (e.g. 2.5 min). Furthermore, the intermediate products in the treated solution were not found through HPLC in the end. Otherwise, the activated carbon powder as catalyst could be reused through simple treatment. Thus, as a novel technology treating dyestuff wastewaters, the method of microwave irradiation with activated carbon powder adopted as catalyst reveals many advantages, such as complete and rapid degradation, low cost, no intermediate products, no secondary pollution, and so on. Maybe, it is fit for treating those wastewaters containing concentrated azo dyes. In conclusion, the research results demonstrate the feasibilities treating dye wastewaters adopting the method combining microwave radiation with activated carbon catalyst in the future.

Acknowledgements

The authors greatly acknowledge The National Natural Science Foundation of China for financial support. The authors also thank our colleagues and other students participating in this work.

References

- D. Rajkumar, J.G. Kim, Oxidation of various reactive dyes with in situ electro-generated active chlorine for textile dyeing industry wastewater treatment, J. Hazard. Mater. 136 (2003) 203–212.
- [2] F.I. Hai, K. Yamamoto, K. Fukushi, Development of a submerged membrane fungi reactor for textile wastewater treatment, Desalination 192 (2006) 315–322.
- [3] J.S. Chang, Y.C. Lin, Fed-batch bioreactor strategies for microbial decolorization of azo dye using a *Pseudomonas luteola* strain, Biotechnol. Prog. 16 (2000) 979–985.
- [4] Y.H. Hsien, C.F. Chang, Y.H. Chen, S.F. Cheng, Photodegradation of aromatic pollutants in water over TiO₂ supported on molecular sieves, Appl. Catal. B: Environ. 31 (2001) 241–249.
- [5] U. Zissia, G. Lyberatosa, Axo-dye biodegradation under anoxic conditions, Water Sci. Technol. 34 (1996) 1102–1108.
- [6] G. Annadurai, R.S. Juang, P.S. Yen, D.J. Lee, Use of thermally treated waste biological sludge as dye absorbent, Adv. Environ. Res. 7 (2003) 739–744.

- [7] H.Q. Zhan, H. Tian, Photocatalytic degradation of acid azo dyes in aqueous TiO₂ suspension. I. The effect of substituents, Dyes Pigments 37 (1998) 231–239.
- [8] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard, J.M. Herrmann, Photocatalytic degradation of various types of dyes (alizarin S, crocein orange G, methyl red, congo red, methylene blue) in water by UV-irradiated titania, Appl. Catal. B: Environ. 39 (2002) 75–90.
- [9] M.S. Khehra, H.S. Saini, D.K. Sharma, B.S. Chadha, S.S. Chimni, Biodegradation of azo dye C.I. acid red 88 by an anoxic–aerobic sequential bioreactor, Dyes Pigments 70 (2006) 1–7.
- [10] T. Matthew, A. John, Bumpus biodegradation of congo red by phanerochaete chrysosporium, Water Res. 32 (1998) 1713–1717.
- [11] T. Sauer, G. Cesconeto Neto, H.J. José, R.F.P.M. Moreira, Kinetics of photocatalytic degradation of reactive dyes in a TiO₂ slurry reactor, J. Photochem. Photobiol. A: Chem. 149 (2002) 147–154.
- [12] P. Piccinini, C. Minero, M. Vincenti, E. Pelizzetti, Photocatalytic mineralization of nitrogen-containing benzene derivatives, Catal. Today 39 (1997) 187–195.
- [13] I. Safarik, M. Safankova, Detection of low concentrations of malachite green and crystal violet in water, Water Res. 36 (2002) 196–200.
- [14] I. Polaert, L. Estel, A. Ledoux, Microwave-assisted remediation of phenol wastewater on activated charcoal, Chem. Eng. Sci. 60 (2005) 6354– 6359.
- [15] L.L. Bo, X. Quan, S. Chen, H.M. Zhao, Y.Z. Zhao, Degradation of *p*nitrophenol in aqueous solution by microwave assisted oxidation process through a granular activated carbon fixed bed, Water Res. 40 (2006) 3061–3068.
- [16] Z.H. Ai, P. Yang, X.H. Lu, Degradation of 4-chlorophenol by microwave irradiation enhanced advanced oxidation processes, Chemosphere 60 (2005) 824–827.

- [17] X. Quan, X.T. Liu, L.L. Bo, S. Chen, Y.Z. Zhao, X.Y. Cui, Regeneration of acid orange 7-exhausted granular activated carbons with microwave irradiation, Water Res. 38 (2004) 4484–4490.
- [18] S. Senthilkumaar, P. Kalaamani, K. Porkodi, P.R. Varadarajan, C.V. Subburaam, Adsorption of dissolved reactive red dye from aqueous phase onto activated carbon prepared from agricultural waste, Bioresource Technol. 97 (2006) 1618–1625.
- [19] N.F. Fahim, B.N. Barsoum, A.E. Eid, M.S. Khalil, Removal of chromium(III) from tannery wastewater using activated carbon from sugar industrial waste, J. Hazard. Mater. B 136 (2006) 303–309.
- [20] X.T. Liu, X. Quan, L.L. Bo, S. Chen, Y.Z. Zhao, Simultaneous pentachlorophenol decomposition and granular activated carbon regeneration assisted by microwave irradiation, Carbon 42 (2004) 415–422.
- [21] M.L. Canle, J.A. Santaballa, E. Vulliet, On the mechanism of TiO₂photocatalyzed degradation of aniline derivatives, J. Photochem. Photobiol. A: Chem. 175 (2005) 192–200.
- [22] H.M. Coleman, K. Chiang, R. Amal, Effects of Ag and Pt on photocatalytic degradation of endocrine disrupting chemicals in water, Chem. Eng. J. 113 (2005) 65–72.
- [23] J. Wang, G. Zhang, Z.H. Zhang, X.D. Zhang, G. Zhao, F.Y. Wen, Z.J. Pan, Y. Li, P. Zhang, P.L. Kang, Investigation on photocatalytic degradation of ethyl violet dyestuff using visible light in the presence of ordinary rutile TiO₂ catalyst doped with upconversion luminescence agent, Water Res. 40 (2006) 2143–2150.
- [24] X.W. Zhang, Y.Z. Wang, G.T. Li, J.H. Qu, Oxidative decomposition of azo dye C.I. acid orange 7 (AO7) under microwave electrodeless lamp irradiation in the presence of H₂O₂, J. Hazard. Mater. B134 (2006) 183–189.
- [25] J. Wang, B.D. Guo, X.D. Zhang, Z.H. Zhang, J.T. Han, J. Wu, Sonocatalytic degradation of methyl orange in the presence of TiO₂ catalysts and catalytic activity comparison of rutile and anatase, Ultrason. Sonochem. 12 (2005) 331–337.